EVALUATION OF AMENDMENTS IN THE REHABILITATION OF SULFIDE MINE TAILINGS FROM SÃO DOMINGOS

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1 INTRODUCTION

The São Domingos mining area is located in the Iberian Pyrite Belt, SE Portugal, and represents a serious environmental hazard (Matos and Martins, 2006). Exploitation dated back to pre-roman and roman times with extraction of Ag, Au and Cu exploitation, mainly in the *gossan* (resulting from the ore weathering). The intense exploitation started in the middle of 19th century, both in the *gossan* and sulfide ore-containing Cu, Zn, As and Pb, and lasted until 1960, with the exhaustion of the ore (Quental *et al.*, 2002). Different types of waste materials were left: *gossan*, host rocks (volcanic with shales, and shales), roman and modern slags, smelting ashes and brittle and blocks of pyrite (Matos, 2004; Álvarez-Valero *et al.*, 2008). All sulfide mine wastes are typically heterogeneous and contain high amounts of trace elements, acidic pH and small contents of organic matter and nutrients. The large dumps containing pyrite and other metal sulfides generate, by oxidation, acidic mine drainage (AMD) which increases the availability of trace elements for microorganisms and plants in the surrounding soils. All of these characteristics contribute towards a system that is barely capable of supporting the establishment or survival of plants.

The use of amendments and spontaneous colonization (vegetation) from mining areas (phytostabilization) are cost-effective and environmentally sustainable methods to rehabilitate these contaminated and degraded areas even in arid and semi-arid conditions (Tordoff *et al.*, 2000; Mendez and Maier, 2008). Thus, the preparation of Technosols from mixtures of organic and inorganic wastes can be an attractive option to rehabilitate mining areas because they can improve physical, chemical and biological properties contributing, at the same time, towards a strategy of wastes valorisation (Macías, 2004). The use of mixtures composed of residues with different C:N ratios can be used to manipulate the rate of mineralization. Nevertheless, the amendments used should also promote other soil functions (Arbestain *et al.*, 2008). The objective of this study was to evaluate the influence of cost-effective organic and inorganic amendments, available in the region, in the rehabilitation of sulfide materials from the São Domingos mine area.

2 MATERIALS AND METHODS

2.1 Materials

Composite samples of mine wastes (MW), containing mainly crushed pyrite and smelting ash, were collected in 2009 at the São Domingos mine area. The large volumes present in the mine, the absence of vegetation and the potential risk as a source of contamination were the reasons for choosing this mining waste. The amendments applied were mixtures, at 30 Mg/ha and 75 Mg/ha, containing distinct wastes from: AGR - agriculture (plant remains+strawberry substrate at 40:60 m:m), MED – residue from the distillation of *Arbutus unedo* L. fruit, ALF – residue from distillation of *Ceratonia siliqua* L. fruit and RW - rockwool (used for the strawberry crop). Limestone rock wastes (LR) were also added at 55 Mg/ha. These organic and inorganic wastes were used due to their characteristics and their presence in large quantities and at “zero cost” in the vicinity of the mine.

2.2 Methods

Assays were performed in pots with five treatments (four replicates each): a) control with MW only (6 kg); b) MW+LR+Amendment at 30 Mg/ha composed of AGR+MED+RW; c) MW+LR+Amendment at 75 Mg/ha composed of AGR+MED+RW; d) MW+LR+Amendment at 30 Mg/ha composed of AGR+ALF+RW; e) MW+LR+Amendment at 75 Mg/ha composed by AGR+ALF+RW. The tailings were mixed manually with these amendments, potted and then maintained at 70% of water-holding capacity in a greenhouse. After one and four months of incubation, samples were collected from each pot (0-5 cm of depth).

Multi-elemental analysis of the initial mining wastes (total) and organic/inorganic wastes were undertaken by atomic emission spectrometry with induced plasma (ICP-EAS) and instrumental neutron activation analysis (INAA) after acid digestion with $HClO_4$+HNO_3+HCl+HF (Activation Laboratories, 2006).

Samples taken after incubation (fraction <2 mm) were characterized for total organic carbon, extractable P and K and total N (Póvoas and Barral, 1992). All organic and inorganic wastes and initial mine waste materials (<2 mm) were also chemically characterized for the same parameters using the same methodologies. Electric conductivity (Ec) and pH were analysed in a water suspension 1:10 (DIN method, 1984) which is representative of the leachate. The dehydrogenase enzyme activity was analyzed according to Tabatai (1994).

3 RESULTS AND DISCUSSION

São Domingos mining wastes are characterised by pH~2, a large Ec (7.35 to 7.49 mS/cm) and low fertility (Table 1). These properties, together with the large total concentrations of hazardous elements (As: 1.1 g/kg; Al: 58.1 g/kg; Cr: 76.7 mg/kg; Cu: 2.1 g/kg; Hg: 75 mg/kg; Pb: 11.7 g/kg; S: 65.3 g/kg; Zn: 1.1 g/kg) explain the absence of vegetation and natural colonization. These properties and chemical composition are associated with the character of the wastes where sulfide materials and potential AMD are present. All the organic and inorganic wastes used as amendments had chemical characteristics considered beneficial and safe for land application and rehabilitation of mining wastes: pH >4.91, small Ec and large concentrations of organic matter and nutrients (Table 1). The concentrations of trace elements were small (data not shown).

TABLE 1 **Chemical characterization of organic and inorganic wastes used as amendments and mining wastes from São Domingos mine area**

Wastes	pH	Ec (mS/cm)	Extractable P (mg/kg)	Extractable K (mg/kg)	Total N (g/kg)	Organic matter (g/kg)
AGR (Plant remains)	7.18	3.47	3145.30	6557	19.18	593
AGR (Strawberry substrate)	6.62	0.91	342.35	166	10.94	653
RW	7.08	3.50	7922.12	730.4	12.90	146
MED	4.91	1.74	175.53	3569	9.26	146
ALF	6.10	0.24	117.28	9130	13.39	945
MW	2.11-2.31	7.35-7.49	< Ld	16.6-58.1	1.96-1.98	113-138

AGR: agriculture (plant remains+strawberry); RW: rockwool; MED: residue from the distillation *Arbutus unedo* L. fruit; ALF: residue from the distillation *Ceratonia siliqua* L. fruit; MW: mining wastes; Ld: Limit of detection

After one month of incubation, the pH increased with amendments from ~2 (control and initial value in MW), to values between 3.78 and 5.06. The treatments at 75 Mg/ha resulted in greater pH than those at 30 Mg/ha, independently of the organic wastes included in the amendment (MED or ALF). After four months of incubation, the pH decreased back to values similar to those measured at the beginning of the experiment. Limestone rock wastes were the main cause for the pH increase in the first month of incubation however the continued acidification, due to sulfides oxidation, promoted the rapid solubilization of carbonates. All the treatments had smaller Ec values

(1.90-2.88 mS/cm and ~4 mS/cm after one and four months of incubation, respectively) than initial mining wastes (7.35-7.49 mS/cm).

The concentrations of extractable P increased in amended treatments from one to four months of incubation, especially with the application of AGR+MED+RW at 75 Mg/ha (102.45 mg/kg, Figure 1). The increased concentration of extractable P in control compared to the initial mine material, can be attributed to the generation of AMD and consequently the increased solubilization of solid phases containing P. Extractable K increased from one to four months in the control, but the amendments had little effect on this nutrient (Figure 1). Potassium leaching to deeper layers or its unavailability due to amendments application can be reasons for the decrease of this element in the soil surface layer (compared to initial values of MW). Total N was similar in all treatments and sampling periods (1.96-2.64 g/kg).

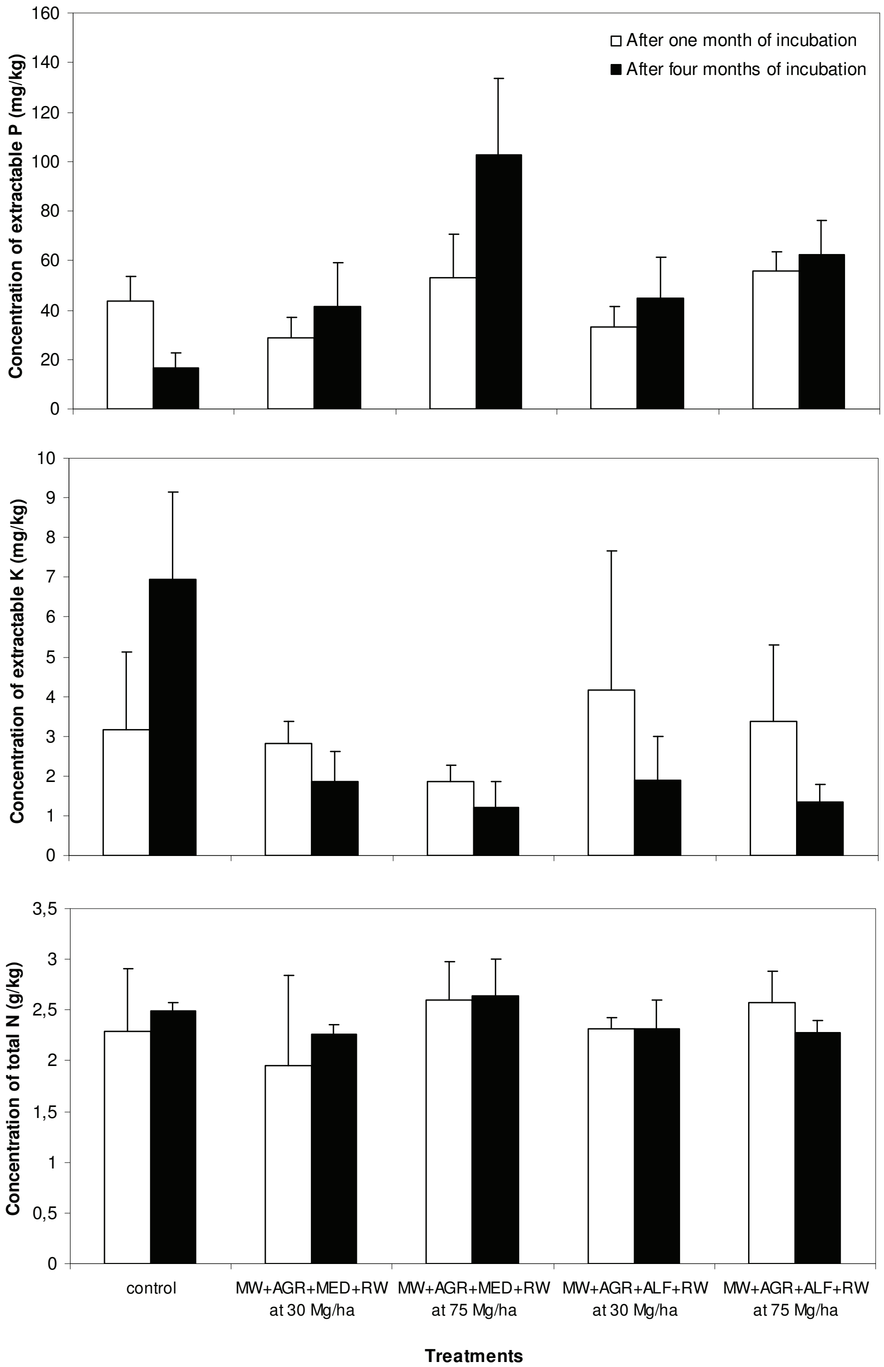

FIGURE 1 **Concentrations of extractable P and K and total N of different treatments after one and four months of incubation (media±SD, *n*=4)**

The dehydrogenase activity was very small in all amended treatments and in both sampling periods (0.25-0.61 µg triphenylformazan (TPF). g dry weight 16 h^{-1}) but the values in second sampling date were twice those of first date, except with application of amendment at 30 Mg/ha composed by AGR+ALF+RW. After the first month of incubation, the control had the greatest dehydrogenase activity (1.19 µg TPF g dry weight 16 h^{-1}), but after four months it was below the detection limit of the methodology. The application of amendment with residue from distillation of *Ceratonia siliqua* fruit (ALF), principally at 75 Mg/ha after four months of incubation, presented the higher dehydrogenase activity (0.61 µg dry weight 16 h^{-1}) than other amended treatments.

4 CONCLUSIONS

Mine wastes, composed predominantly of sulfide containing materials, present a serious environmental risk due to the large concentrations of trace elements and continued generation of acid mine drainage. The amendments tested were, in general, similar in their effect and did not increase, adequately, the fertility of this waste. The application rate of amendments should be greater than 75 Mg/ha and combined with other wastes capable of increasing pH but with a small dissolution rate and, therefore, more persistent. The amendments had only a small effect on microbial activity (measured by dehydrogenase) and the activity of the native microbial community was very small, as would be expected in such extreme conditions. It is clear from the results that amendment application per se will be insufficient to allow the establishment of a permanent vegetation cover. Some barrier to prevent impact of underlying layers will be needed, to prevent the impact (namely of acidic salts) on the amended surface layer, however more investigation is needed.

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